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alloy texture an alloy or an intermetallic compound with Bi and Pb existing either in independent states or in a mutually joined state, thereby mending the deterioration of the tensile strength at elevated temperatures.

Disclosure of the Invention:

A copper-based alloy contains Bi and Pb and has 0.01 to 1.0 weight% of Te incorporated therein as an additive element to form in an alloy texture an intermetallic compound of Pb-Te having a higher melting point than a Bi-Pb binary eutectic crystal, suppress occurrence of the Bi-Pb binary eutectic crystal in the alloy texture and improve mechanical properties, particularly tensile strength, thereof at elevated temperatures.

In the copper-based alloy, the additive element is contained in a ratio of 0.01 to 0.22 weight%.

In the copper-based alloy, it contains at least Sn in a ratio of 2.8 to 6.0 weight%, Zn in a ratio of 1.0 to 12.0 weight% and Bi in a ratio of 0.1 to 3.0 weight%.

In the copper-based alloy, wherein it contains at least Sn in a ratio of 2.8 to 6.0 weight%, Zn in a ratio of 1.0 to 12.0 weight%, Bi in a ratio of 0.1 to 2.4 weight% and Se in a ratio of 0.05 to 1.2 weight%.

In the copper-based alloy, it has a Pb content of not more than 0.25 weight%.

Brief Description of the Drawing

Fig. 1 is a graph showing the results of tensile test 1.

Fig. 2 is a graph showing the results of tensile test 2.

Fig. 3 is a graph showing the results of tensile test 3.

Fig. 4 is a graph showing the results of tensile test 3.

Fig. 5 is a graph showing the results of tensile test 3.

Fig. 6 is a graph showing the results of tensile test 4.

Fig. 7 is a graph showing the results of a machinability test.

Fig. 8 is a graph showing the results of the Charpy impact test of samples, No.62 to No. 64, and the surface area ratio of Bi-Pb.

Fig. 9 is a graph showing the results of the Charpy impact test of samples, No. 65

to No. 67, and the surface area ratio of Bi-Pb.

Fig. 10 is a metallographic photograph (400 magnifications) of a standard sample (comparative example).

Fig. 11 is a mapping of the component elements appearing in the metallographic photograph of Fig. 10.

Fig. 12 is a metallographic photograph (400 magnifications) of sample No. 63 containing P in a ratio of 0.09 weight%.

Fig. 13 is a mapping of the component elements appearing in the metallographic photograph of Fig. 12.

Fig. 14 is a metallographic photograph (400 magnifications) of sample No. 66 containing Te in a ratio of 0.21 weight%.

Fig. 15 is a mapping of the component elements appearing in the metallographic photograph of Fig. 14.

Fig. 16 is a histolytic photograph (before and after image processing) determining the surface area ratios of samples No. 62 to No. 64.

Fig. 17 is a histolytic photograph (before and after image processing) determining the surface area ratios of samples No. 65 to No. 67.

Best Mode for carrying out the Invention:

The significance of using an additive element forming an alloy or an intermetallic compound with Bi and Pb existing either in independent states or in a mutually joined state in the copper-based alloy of this invention will be described below.

When the alloy incorporates Te as an additive element therein, a Pb-Te intermetallic compound (or alloy) is formed to suppress occurrence of Bi-Pb binary eutectic crystal in the alloy texture.

The cast alloy, by containing Te therein as the additive element, is enabled during the course of solidification thereof to form the Pb-Te intermetallic compound (or alloy) having a higher melting point than the Bi-Pb binary eutectic crystal

earlier than the precipitation of the Bi-Pb binary crystal in the alloy texture and consequently decrease the Bi and Pb forming the Bi-Pb binary eutectic crystal in the alloy texture, suppress the occurrence of the Bi-Pb binary eutectic crystal and realize the enhancement of the mechanical properties at elevated temperatures.

The particularly preferred copper-based alloys are Cu-Sn-Zn-Bi- and Cu-Sn-Zn-Bi-Se-based alloys. These copper-based alloys adopt the form of containing the component elements shown below. The individual ranges of these components and the reasons therefor will be specifically described in detail below.

Sn: 2.8 to 6.0 weight%

This element is contained for the purpose of permitting solid solution in the α phase, enhancing strength and hardness and enhancing wear resistance and corrosion resistance owing to the formation of a protective film of SnO_2 . The Sn is an element that in the range of actual ratio in a composition degrades machinability in accordance as the content thereof is increased. It is, therefore, required to secure mechanical properties in the range in which the content is suppressed and further the corrosion resistance is kept from decreasing. As the more preferred range particularly in terms of the characteristic quality of the elongation which is susceptible of the influence of the Sn content, the range of 3.5 to 4.5 weight% in which the elongation in the neighborhood of 4.0 weight% promising the best characteristic properties is infallibly attained has been discovered.

Zn: 1.0 to 12.0 weight%

This element is effective in enhancing hardness and mechanical properties, particularly elongation, without affecting machinability. The content effective in improving characteristic properties at elevated temperatures is found to be not less than 1.0 weight% in consideration of the additive elements, such as Te that forms an alloy or an intermetallic compound with Bi and Pb, and the Sn content. Since the Zn is further effective in suppressing the occurrence of Sn oxide due to the absorption of gas by the melt and ensuring the wholesomeness of the melt, the content of not less than 4.0 weight% is found to be effective in enabling this action to be taken. More practically, the content of not less than 5.0 weight% proves advantageous from the viewpoint of compensating for the proportions of Bi and Se to be suppressed. Since the Zn has a high vapor pressure, the content of not more than 12.0 weight% proves favorable in

to mend the deterioration of tensile strength proportionately to the increase of the content. All these points taken into consideration, the Te content has been specified in the range of 0.01 to 1.0 weight% and preferably in the range of 0.05 to 0.5 weight%.

P: 0.01 to 0.5 weight%

This element is contained in a ratio in the range of 0.01 to 0.5 weight% for the purpose of promoting the deacidification of the melt and successfully manufacturing a wholesome cast alloy. When the content exceeds the upper limit of this range, the excess tends to lower the solidus line and induce segregation. When the P is added as a deacidifying agent, the P content in the alloy generally is in the range of 0.015 to 0.03 weight%. For the purpose of inducing crystallization of an intermetallic compound Pb_3P_2 which has a higher melting point than the Bi-Pb binary eutectic crystal (melting point of about 125°C), suppressing the formation of the Bi-Pb binary eutectic crystal and mending the deterioration of the tensile strength at elevated temperatures, the content is preferred to be in the range of 0.05 to 0.1 weight%.

Pb: not more than 0.25 weight%

In view of the possibility that the Pb is contained in a ratio in the range of 0.3 to 0.4 weight% even on the impurity level, the content of the Pb as not a positively admissible unavoidable impurity is specified to be not more than 0.25 weight%.

Besides the Te mentioned above, the additive element that the copper-based alloy of this invention is allowed to use for the purpose of suppressing the occurrence of the Bi-Pb binary eutectic crystal is one or more members selected from the group consisting of Te, P, Zr, Ti, Co, In, Ca, B and misch metal. The content of the additive element is preferred to be in the range of 0.01 to 1.0 weight%.

The cast alloy, by containing the additive element, is enabled during the course of solidification thereof to form a Bi-M intermetallic compound (or alloy), Pb-M intermetallic compound (or alloy) or Bi-Pb-M intermetallic compound (or alloy) having a higher melting point than Bi-Pb binary eutectic crystal earlier than the precipitation of the Bi-Pb binary crystal in the alloy texture and consequently decrease the Bi and Pb forming the Bi-Pb binary eutectic crystal in the alloy texture and suppress the occurrence of the Bi-Pb binary eutectic crystal.

Incidentally, the M denotes the additive element, and by suppressing the occurrence of Bi-Pb binary eutectic crystal, the mechanical properties at elevated temperatures can be enhanced. As regards the copper-based alloy containing Sb at a

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ratio in the range of 0.05 to 0.5 weight%, the use of the aforementioned additive elements is effective in suppressing the occurrence of the Bi-Pb binary eutectic crystal and enhancing the characteristic properties at elevated temperatures. As concrete examples of the unavoidable impurities in the copper-based alloy of this invention, Fe (not more than 0.3 weight%), Al (not more than 0.01 weight%), and Si (not more than 0.01 weight%) may be cited.

In the leadless copper-based alloys conforming to this invention, the Cu-Sn-Zn-Bi-Se- and the Cu-Sn-Zn-Bi-based bronze cast alloys containing Te and Zr as added elements were tested for tensile strength. The results of the test will be described below.

The tensile test was performed on a test piece No. 4 specified in JIS (Japanese Industrial Standard) Z2201 and manufactured by casting a given sample in a CO₂ mold at a casting temperature of 1130°C in accordance with the JIS A Plan and cutting the resultant molding alloy by using an Amsler's tensile tester. This tensile test was carried out on individual samples of n = 4. The test results reported are averages of the numerical values found for these samples.

The four tensile tests were carried out each under the following four conditions.

(Test 1)

Te content: 0.04 to 1.48 weight% (this invention), Testing temperatures: room temperature (22°C), 100°C and 150°C. The compositions of samples were as shown in Table 1. This test 1 was intended to confirm the effect of the Te content.

Table 1

Sample		Chemical analyses (unit: weight%)							
		Cu	Zn	Sn	Bi	Se	Pb	P (ppm)	Te
Comp. Example	No. 1	86.3	8.16	4.16	1.17	0.15	0.005	194	0
This invention	No. 2	85.9	8.28	4.36	1.19	0.19	0.006	199	0.04
This invention	No. 3	86.1	8.33	4.19	1.17	0.19	0.004	182	0.11
This invention	No. 4	86.0	8.30	4.28	1.22	0.18	0.004	193	0.16
This invention	No. 5	85.7	8.06	4.17	1.28	0.20	0.005	232	0.50
This invention	No. 6	85.1	8.27	4.09	1.30	0.20	0.004	190	0.99
This invention	No. 7	84.7	8.14	4.11	1.32	0.21	0.004	216	1.48

(Test 2)

Te content: 0.04 to 0.17 weight% (this invention), Se content: 0 to 1.2 weight%, Testing temperature: 150°C. The compositions of samples were as shown in Table 2. This test 2 was intended to confirm the effect of the Te content by using samples of varied Se contents.

Table 2

Sample		Chemical analyses (unit: weight%)							
		Cu	Zn	Sn	Bi	Se	Pb	P (ppm)	Te
Comp. Example	No. 8	86.4	8.30	3.91	1.2	0	0.0105	196	0
Comp. Example	No. 9	85.9	8.18	4.24	1.38	0.21	0.0094	207	0
Comp. Example	No. 10	85.6	8.32	4.21	1.36	0.42	0.0121	216	0
Comp. Example	No. 11	85.2	8.50	4.13	1.41	0.65	0.0095	190	0
Comp. Example	No. 12	85.1	8.14	4.05	1.4	1.18	0.0099	230	0
This invention	No. 13	86.4	8.32	3.98	1.25	0	0.0096	209	0.06
This invention	No. 14	85.8	8.30	4.12	1.34	0.22	0.0112	201	0.06
This invention	No. 15	85.3	8.30	4.27	1.48	0.50	0.0106	218	0.04
This invention	No. 16	85.7	8.24	4.02	1.36	0.60	0.008	208	0.05
This invention	No. 17	85.3	8.21	3.91	1.42	1.13	0.0092	223	0.06
This invention	No. 18	86.4	8.30	3.98	1.21	0.01	0.0097	206	0.11
This invention	No. 19	86.2	8.22	4.02	1.27	0.21	0.0105	226	0.1
This invention	No. 20	86.0	8.16	4.02	1.3	0.43	0.0135	205	0.12
This invention	No. 21	86.2	7.99	3.96	1.22	0.58	0.0104	203	0.1
This invention	No. 22	84.9	8.38	4.09	1.36	1.20	0.0162	216	0.11
This invention	No. 23	86.6	8.35	3.82	1.23	0	0.0147	208	0.14
This invention	No. 24	86.5	7.95	4.03	1.27	0.21	0.0055	208	0.14
This invention	No. 25	85.7	8.14	4.25	1.36	0.42	0.0144	207	0.15
This invention	No. 26	85.5	8.25	4.08	1.43	0.64	0.0141	213	0.17
This invention	No. 27	85.0	8.17	4.16	1.41	1.18	0.0118	225	0.15

(Test 3)

Te content: 0.09 to 0.22 weight% (this invention), Se content: 0 to 0.83 weight%, Zn content: 1.02 to 8.53 weight%, Testing temperature: 150°C. The compositions of samples were as shown in Table 3. This test 3 was intended to confirm application to low Zn.

Table 3

Sample		Chemical analyses (unit: weight%)							
		Cu	Zn	Sn	Bi	Se	Pb	P (ppm)	Te
Comp. Example	No. 28	91.8	1.90	4.57	1.72	0.01	0.0211	182	0
This invention	No. 29	91.8	1.93	4.46	1.73	0.00	0.0200	203	0.12
This invention	No. 30	91.8	1.71	4.61	1.82	0.45	0.0188	153	0.21
Comp. Example	No. 31	91.2	1.97	4.59	1.79	0.45	0.0175	210	0
This invention	No. 32	91.2	1.99	4.34	1.76	0.43	0.0165	238	0.10
This invention	No. 33	92.4	1.02	4.54	1.81	0.82	0.0267	146	0.21
Comp. Example	No. 34	91.4	1.44	4.43	1.79	0.79	0.0271	211	0
This invention	No. 35	91.3	1.76	4.42	1.68	0.83	0.0169	278	0.09
This invention	No. 36	91.4	1.48	4.57	1.83	0.02	0.0169	226	0.22
Comp. Example	No. 37	90.1	3.58	4.62	1.69	0.01	0.0180	234	0
This invention	No. 38	90.2	3.44	4.47	1.66	0.01	0.0185	229	0.12
This invention	No. 39	90.1	3.66	4.57	1.63	0.38	0.0260	206	0.22
Comp. Example	No. 40	89.6	3.73	4.42	1.72	0.41	0.0186	234	0
This invention	No. 41	89.8	3.70	4.54	1.63	0.41	0.0155	225	0.13
This invention	No. 42	89.6	3.80	4.42	1.62	0.78	0.0162	242	0.21
Comp. Example	No. 43	89.8	3.25	4.39	1.69	0.75	0.0209	217	0
This invention	No. 44	89.4	3.66	4.52	1.70	0.77	0.0142	242	0.12
This invention	No. 45	89.2	3.71	4.54	1.71	0.01	0.0174	210	0.20
Comp. Example	No. 46	85.8	8.12	4.56	1.48	0.00	0.0168	246	0
This invention	No. 47	85.4	8.53	4.22	1.42	0.00	0.0150	232	0.10
This invention	No. 48	86	8.45	4.51	1.27	0.33	0.101	226	0.22
Comp. Example	No. 49	85.1	8.45	4.42	1.53	0.32	0.143	264	0
This invention	No. 50	85.4	8.38	4.42	1.45	0.28	0.139	261	0.11
This invention	No. 51	85.5	8.36	4.54	1.35	0.28	0.123	249	0.22
Comp. Example	No. 52	84.9	8.38	4.54	1.54	0.60	0.137	262	0
This invention	No. 53	85	8.34	4.43	1.51	0.64	0.139	262	0.13
This invention	No. 54	85	8.26	4.51	1.56	0.58	0.142	277	0.21

(Test 4)

Zr content: 0.05 to 0.21 weight%, Testing temperature: room temperature (20°C), 100°C and 150°C. The compositions of samples were as shown in Table 4. This test 4 was intended to confirm the effect of Zr content.

For the purpose of determining the ratio of the areas of a Bi-Pb binary eutectic crystal, the metallographic photograph was entrapped and analyzed by the image analyzing software.

The term “ratio of areas” refers to the ratio of an area occupied by a target (the Bi-Pb binary eutectic phase) to the area of the field of view formed of the entrapped image.

The Bi-Pb binary eutectic phase was identified through comparison between the results of the EDX quantitative analysis and the metallographic photograph. The metallographic photograph was obtained in 400 magnifications and the ratio of areas was obtained by calculating the average values of 20 fields of vision of each of the samples.

The texture observation photographs (before and after image processing) portraying the ratios of areas of the standard sample (sample No. 64), the sample No. 62 containing P in a ratio of 0.05 weight% and the sample No. 63 containing P in a ratio of 0.09 weight% are shown in Fig. 16. The results of the determination of the ratios of areas of the Bi-Pb binary eutectic crystal formed in the case of containing P as an additive element are shown in Table 12.

The texture observation photographs (before and after image processing) portraying the ratios of areas of the standard sample (sample No. 67), the sample No. 65 containing Te in a ratio of 0.1 weight% and the sample No. 66 containing Te in a ratio of 0.21 weight% are shown in Fig. 17. The results of the determination of the ratios of areas of the Bi-Pb binary eutectic crystal formed in the case of containing Te as an additive element are shown in Table 12.

As shown in Table 12, the ratio of areas of the Bi-Pb phase of the standard sample (sample No. 64) was 0.268% and the ratio of areas of the Bi-Pb phase containing P was 0.103% when the P content was 0.05 weight% and 0.104% when the P content was 0.09 weight%. The data of these samples No. 62 to No. 64 plotted in a graph is shown in Fig. 8.

As shown in Table 12, the ratio of surfaces of the Bi-Pb phase of the standard sample (the sample No. 67) was 0.212% and the ratio was 0.052% when the Te content was 0.1 weight% and 0.035% when the Te content was 0.21 weight%. The data of these samples No. 65 to 67 plotted in a graph are shown in Fig. 9.

Fig. 8 and Fig. 9 reveal that the containment of P and Te as additive elements resulted in suppressing the ratio of areas of the Bi-Pb phase below 0.2%. They also

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reveal that the suppression of the occurrence of the Bi-Pb binary eutectic crystal